



Recent progress on process integration of the Ca-Cu technology for decarbonization of ammonia, iron and steel and hydrogen industries

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Abstract

The production of hydrogen via natural gas reforming or water gas shift in the presence of a CaO-based material has received great attention over a long period due to its great potential in terms of energy efficiency and CO₂ capture efficiency compared to other low-carbon emission hydrogen production processes. The regeneration of the CaCO₃ formed during the hydrogen production step by means of a second redox loop of Cu/CuO was proposed almost a decade ago in order to boost the efficiency of the process, while avoiding the highly energy-demanding oxygen-fired regeneration step. Since then, this Ca-Cu process has noticeably progressed [1], being recently demonstrated at TRL4 under the FP7 project ASCENT [2].

Hydrogen production in a series of fixed bed reactors is the Ca-Cu process configuration that has been mostly assessed due to its inherent advantage of allowing pressure swing between the high pressure sorption enhanced reforming stage for hydrogen production and the low pressure CaCO₃ regeneration step. A further advantage of integration of the Ca-Cu technology in hydrogen plants compared to power generation is that carbon-rich PSA off-gases can be used in the sorbent regeneration step leading to virtually zero-emission plants. Different fixed bed reactors configurations, operating conditions and fuel properties have been widely studied in the literature making use of reactor models with different levels of complexity [3-6]. Hydrogen production efficiencies that are noticeably higher than those obtained with commercial steam reformers have been demonstrated for this Ca-Cu process (i.e. 7-8%points), even when accounting for the electricity consumption associated with the production of a rich-CO₂ stream ready for compression and storage [4].

Considering the inherent co-production of a high pressure N_2 -rich stream as one of its products, the integration of the Ca-Cu process in ammonia plants has been recently assessed [7]. The conceptual scheme shown in Fig. 1 shows the proposed process integration, where the H_2 - and N_2 -rich gas streams produced are purified in two different PSA units and fed to the ammonia synthesis reactor. It has been estimated that the overall specific primary energy consumption per unit of NH_3 produced can be reduced, despite the higher electric consumption associated with the Ca-Cu process. Moreover, the purity of the H_2 and N_2 streams produced in the Ca-Cu looping process would simplify the ammonia production loop, increasing the NH_3 yield per pass in the synthesis reactor and thereby reducing the recycle needs in such reactor [7].

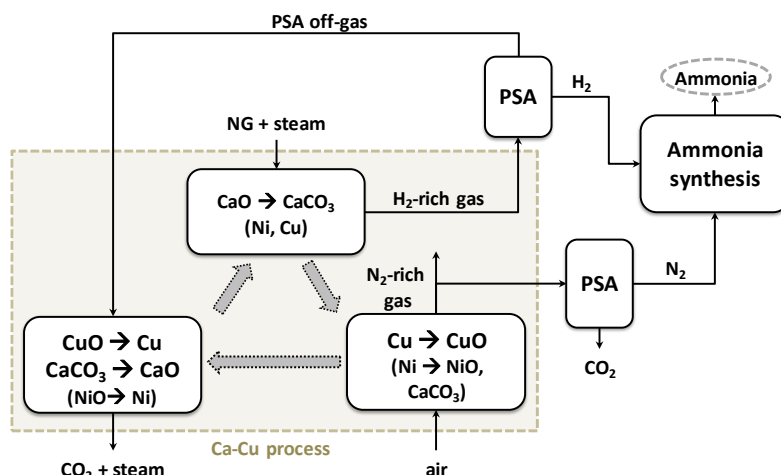


Fig.1 Conceptual scheme of the Ca-Cu process integrated with ammonia synthesis [7]

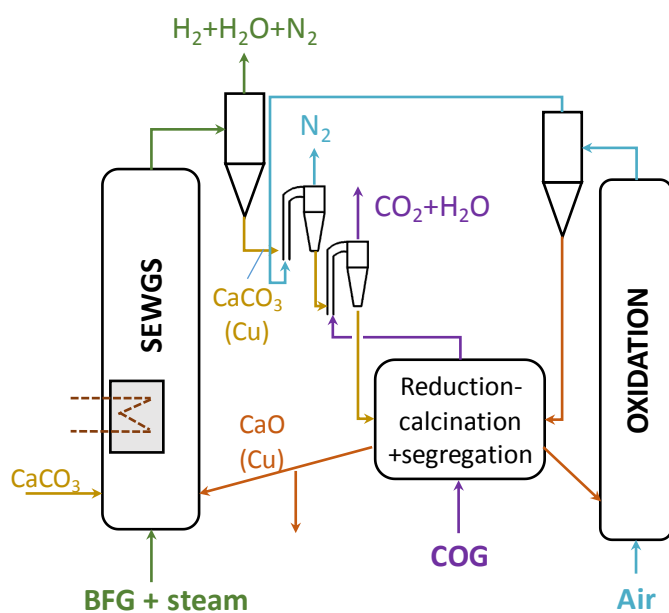


Fig.2 Arrangement of Ca-Cu process reactors for the production of a H_2 -enriched gas from BFG in steel mills

The Ca-Cu looping process has been recently proposed also for the production of a H_2 -enriched fuel gas through sorption enhanced water gas shift (SEWGS) of blast furnace (BFG) gas in steel mills [8]. An arrangement of interconnected fluidized-bed reactors at atmospheric pressure has been proposed in this case, including a solids' segregation step to reduce the solids circulation between the reactors (Fig.2). A N_2 -free fuel gas containing H_2 , CO and/or CH_4 is used as a reducing gas in the reduction/calcination stage, so that the CO_2 produced from the calcination of the $CaCO_3$ is easily purified. The coke oven gas (COG) available in the steel mill, which is rich in H_2 and CH_4 , is proposed for this purpose as shown in Fig. 2. Around 30% of the BFG can be decarbonized in the SEWGS reactor if COG is fed to the reducer/calciner, which can be increased up to 100% if additional

natural gas is used as fuel in the reduction/calcination reactor together with the COG.

In this work, a review of the most recent process advancements published in the literature on the Ca-Cu process for industrial applications is carried out, highlighting the potential of each application, comparing their performance with benchmark processes and discussing the open research questions.

References

- [1] Fernández JR, Abanades JC. Current opinion in chemical engineering 2017, 17: 1–8
- [2] Fernández JR, Alarcón JM, Abanades JC. Ind Eng Chem Res 2016, 55:5128–5132
- [3] Fernández JR, Abanades JC, Murillo R, Grasa G. Int J Greenh Gas Con. 2012, 6:126–141

- [4] Martínez I, Romano MC, Fernández JR, Chiesa P, Murillo R, Abanades JC. Appl Energ 2014, 114:192–208
- [5] Martini M, Martínez I, Romano MC, Chiesa P, Gallucci F, van Sint Annaland M. Chem Eng J 2017, 328:304-319
- [6] Fernández JR, Abanades JC. Chem Eng Sci 2017, 166: 144-160
- [7] Martínez I, Armaroli D, Gazzani M, Romano MC: Ind Eng Chem Res 2017, 56(9):2526-2539
- [8] Fernández JR, Martínez I, Abanades JC, Romano MC. Int J Hydrog Energ 2017, 42 (16):11023-11037